

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

| | | | |
|---|---|---|---|
| Applicant's or agent's file reference SBU 114-WO NP | FOR FURTHER ACTION | | See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416) |
| International application No. PCT/EP99/07691 | International filing date (day/month/year) 13/10/1999 | Priority date (day/month/year) 26/10/1998 | |
| International Patent Classification (IPC) or national classification and IPC C08J9/14 | | | |
| Applicant BAYER AKTIENGESELLSCHAFT et al. | | | |


1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 6 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

| | |
|---|--|
| Date of submission of the demand 13/04/2000 | Date of completion of this report 18.12.2000 |
| Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465 | Authorized officer olde Scheper, B Telephone No. +49 89 2399 2141 |



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP99/07691

i. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).):*

Description, pages:

1-13 as originally filed

Claims, No.:

1-4 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP99/07691

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

| | |
|-------------------------------|-----------------|
| Novelty (N) | Yes: Claims 4 |
| | No: Claims 1-3 |
| Inventive step (IS) | Yes: Claims |
| | No: Claims 4 |
| Industrial applicability (IA) | Yes: Claims 1-4 |
| | No: Claims |

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP99/07691

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

- D1: DE 197 08 570 A (BASF AG) 10 September 1998 (1998-09-10)
- D2: US-A-4 275 172 (BARTH BRUCE P ET AL) 23 June 1981 (1981-06-23)
- D3: US-A-3 821 130 (BARRON B ET AL) 28 June 1974 (1974-06-24)

The document D3 was not cited in the international search report.

1. The present application relates to a method of preparing a rigid polyurethane foam (claims 1-3) and an apparatus for preparing said foam used in the claimed method (claim 4).
2. D1 discloses a method for preparing rigid polyurethane foams in which components (1) to (4) are used wherein the blowing agent is cyclopentane and water and wherein the cyclopentane is mixed in a polyol premix comprising components (2) to (4) (see comparative examples 1 and 6; page 6, line 66 to page 7, line 4; page 8, lines 19-23).

The only difference between present application and D1 appears to be the feature "the polyol (2) is a polyether polyol and/or polyester polyol having poor compatibility with cyclopentane". The feature "poor compatibility" is unclear (see Item VIII below) and an unclear feature cannot establish novelty.

The present application and in particular claims 1 and 3, lack as a consequence novelty (Art. 33(2) PCT).

3. It should be noted that in all examples of D1 (both comparative and according to the disclosed invention) the component A is premixed. At page 7, lines 2-4 it is expressed verbatim disclosed that a static mixer can be used for this purpose. Since component A is always premixed in all examples only one selection need to be made in order to arrive to a method in which a static mixer is used and the application and in particular claim 2, lacks novelty as a consequence (Art. 33(2)

PCT).

4. It should be noted that a claim to a substance or composition for a particular use should be construed as meaning a substance or composition which is in fact suitable for the stated use; a known product which prima facie is the same as the substance or composition defined in the claim, but which is in a form which would render it unsuitable for the stated use, would not deprive the claim of novelty, but if the known product is in a form in which it is in fact suitable for the stated use, though it has never been described for that use, it would deprive the claim of novelty (PCT Guidelines C-III, 4.8).

D2 (column 3, lines 13-45) and D3 (column 2, lines 7-48) disclose the subject-matter of claim 4 but for the circumferential speed of the stirrer of a polyol tank of at least 0.5 m/s.

As far as known to the authorized officer such (premix) tanks are always equipped with a stirrer and the claimed circumferential speed is quit low, therefore common. Even if novelty must be acknowledged for formal reasons no inventive step can be acknowledged. It cannot be derived from the description as filed what problem is solved by such distinguishing feature (Art. 33(3) PCT).

5. Table 1 of the present application shows clearly that the properties of Comparative Example 1 are comparable, or even within the margin of error, of those of Examples 1-3. The thermal conductivity of Comparable Example 2 may be higher, but it should be noted that the composition of the blowing agent is significant changed.
It appears from Table 1 that the claimed subject-matter does not solve any problem.
6. The present application satisfies the criterion set forth in Article 33 (4) PCT because the subject matter of Claims 1-4 is industrially applicable.

Re Item VII

Certain defects in the international application

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP99/07691

1. The application as filed does not contain any clear reference to existing prior art. According to the requirements of Rule 5.1(a)(ii) PCT the applicant is obliged to furnish, according to the best of his knowledge, a true presentation of existing prior art.

Re Item VIII

Certain observations on the international application

1. The feature "poor compatibility" used in claim 1 is unclear (Art. 6 PCT), since there is no unitary, generally accepted method known to the authorized officer which defines said feature.

At page 3, lines 1-4 a definition is provided for the objected feature. Said definition is however coupled with a certain method of measurement disclosed at page 9, lines 6-11. These definitions are not incorporated in claim 1, which is essential since the objected feature appears to be the only feature which might distinguish the claim from the prior art.

2. It is further unclear how said test (page 9, lines 6-11), in which a mixture is allowed to stand for a day, can have any eloquence on a process in which products are intensively mixed and used (almost) immediately.

TENT COOPERATION TREA /

PCT

NOTIFICATION RELATING TO PRIORITY CLAIM

(PCT Rules 26bis.1 and 26bis.2 and
Administrative Instructions, Sections 402 and 409)

From the INTERNATIONAL BUREAU

To:

BAYER AKTIENGESELLSCHAFT
D-51368 Leverkusen
ALLEMAGNE

| | |
|--|--|
| Date of mailing (day/month/year) 28 January 2000 (28.01.00) | |
| Applicant's or agent's file reference SBU 114-WO | IMPORTANT NOTIFICATION |
| International application No. PCT/EP99/07691 | International filing date (day/month/year) 13 October 1999 (13.10.99) |
| Applicant BAYER AKTIENGESELLSCHAFT et al | |

The applicant is hereby **notified** of the following in respect of the priority claim(s) made in the international application.

1. ☒ **Correction of priority claim.** In accordance with the applicant's notice received on: 25 January 2000 (25.01.00), the following priority claim has been corrected to read as follows:

JP 26 October 1998 (26.10.98) 10-303794

- ☐ even though the indication of the number of the earlier application is missing.
☐ even though the following indication in the priority claim is not the same as the corresponding indication appearing in the priority document:

2. ☐ **Addition of priority claim.** In accordance with the applicant's notice received on: , the following priority claim has been added:

- ☐ even though the indication of the number of the earlier application is missing.
☐ even though the following indication in the priority claim is not the same as the corresponding indication appearing in the priority document:

3. ☐ As a **result of the correction and/or addition** of (a) priority claim(s) under items 1 and/or 2, the (earliest) priority date is:

4. ☐ **Priority claim considered not to have been made.**

- ☐ The applicant failed to respond to the Invitation under Rule 26bis.2(a) (Form PCT/IB/316) within the prescribed time limit.
☐ The applicant's notice was received after the expiration of the prescribed time limit under Rule 26bis.1(a).
☐ The applicant's notice failed to correct the priority claim so as to comply with the requirements of Rule 4.10.

The applicant may, before the technical preparations for international publication have been completed and subject to the payment of a fee, request the International Bureau to publish, together with the international application, information concerning the priority claim. See Rule 26bis.2(c) and the PCT Applicant's Guide, Volume I, Annex B2(IB).

5. ☐ In case where **multiple priorities** have been claimed, the above item(s) relate to the following priority claim(s):

6. A copy of this notification has been sent to the receiving Office and

- ☒ to the International Searching Authority (where the international search report has not yet been issued).
☒ the designated Offices (which have already been notified of the receipt of the record copy).

| | |
|--|------------------------------------|
| The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland | Authorized officer P. Regis |
| Facsimile No. (41-22) 740.14.35 | Telephone No. (41-22) 338.83.38 |

PATENT COOPERATION TREATY

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NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
 United States Patent and Trademark
 Office
 Box PCT
 Washington, D.C.20231
 ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

| | |
|---|---|
| Date of mailing (day/month/year) 18 May 2000 (18.05.00) | |
| International application No. PCT/EP99/07691 | Applicant's or agent's file reference SBU 114-WO |
| International filing date (day/month/year) 13 October 1999 (13.10.99) | Priority date (day/month/year) 26 October 1998 (26.10.98) |
| Applicant CHIBA, Takanori et al | |

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
 13 April 2000 (13.04.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

| | |
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| The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35 | Authorized officer C. Villet Telephone No.: (41-22) 338.83.38 |
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WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | |
|---|-----------|---|
| (51) International Patent Classification ⁷ : C08J 9/14, B29C 44/34, C08J 9/30 // C08L 75/04 | A1 | (11) International Publication Number: WO 00/24813 (43) International Publication Date: 4 May 2000 (04.05.00) |
| (21) International Application Number: PCT/EP99/07691 (22) International Filing Date: 13 October 1999 (13.10.99) (30) Priority Data: 10-303794 26 October 1998 (26.10.98) JP (71) Applicant (for all designated States except US): BAYER AKTIENGESELLSCHAFT [DE/DE]; D-51368 Leverkusen (DE). (72) Inventors; and (75) Inventors/Applicants (for US only): CHIBA, Takanori [JP/JP]; 11-16, Shinkofudai 5-chome, Toyono-cho, Toyono-gun, Osaka 563-0105 (JP). MATSUMOTO, Takuya [JP/JP]; 25-18, Motomachi, Suita, Osaka 564-0031 (JP). KITANO, Keiichi [JP/SG]; 53 Jurong East Avenue 1, #09-06, Pare Oasis 609783, Singapore (SG). (74) Common Representative: BAYER AKTIENGESELLSCHAFT; D-51368 Leverkusen (DE). | | (81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> |
| (54) Title: METHOD OF PREPARING RIGID POLYURETHANE FOAM | | |
| (57) Abstract <p>A method of preparing a polyurethane foam having excellent heat insulating properties is provided. A method of preparing a rigid polyurethane foam from (1) an organic polyisocyanate comprising an aromatic polyisocyanate, (2) a polyol comprising a polyether polyol and/or polyester polyol, (3) a blowing agent, and (4) a surfactant, a catalyst and other auxiliaries, characterized in that the blowing agent (3) is cyclopentane and water, the polyol (2) is a polyether polyol and/or polyester polyol having poor compatibility with cyclopentane, and cyclopentane is mixed and dispersed in a polyol premix comprising the components (2) to (4).</p> | | |

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Method of preparing rigid polyurethane foam

The present invention relates to a method of preparing a rigid polyurethane foam and an apparatus for preparing a rigid polyurethane foam. The rigid polyurethane foam
5 can be used as heat insulation materials for freezer, refrigerator, building and the like.

Rigid polyurethane foams are widely used as heat insulation materials for refrigerator-freezer, for example, refrigerators for household use, since they have a low product density, excellent heat insulating properties and a high mechanical
10 strength.

As blowing agents for preparing the rigid polyurethane foams, chlorofluorocarbons (hereinafter referred to as CFCs), in particular trichlorofluoromethane (CFC-11), have been conventionally used.

15 However, since the CFC-11 blowing agent contains halogens, there is apprehension that it may deplete the ozone layer and cause the environmental issues such as global warming. For the purpose of protecting the global environment, the amounts of production and consumption of CFCs are now under international regulations. In
20 Japan, the production of CFCs had been prohibited by the end of 1995. As substitute new blowing agents, hydrochlorofluorocarbons (HCFCs) having a low ozone depletion potential are used. For example, HCFC-141b (1,1-dichloro-1-fluoroethane), HCFC-22 (chlorodifluoromethane), HCFC-142b (1-chloro-1,1-difluoroethane) have been introduced and applied as blowing agents.

25 However, use of HCFCs, the substitute for CFCs, are now phased down, because they also contain chlorine atom in their molecules and therefore still retain the property of depleting the ozone layer although their effects on the ozone layer are little. Thus, in terms of global environmental protection, use of blowing agents
30 having no effects on the ozone layer depletion at all was newly proposed. Hydrocarbon-based blowing agents which contain no chlorine atom and pose no risk

of depleting the ozone layer, for example cyclopentane, have already been introduced and applied for some purposes.

However, although cyclopentane is most suitable as an earth-friendly blowing agent, it involves some drawbacks. In particular, gaseous cyclopentane itself has a high thermal conductivity and the heat insulating performance of the rigid polyurethane foams employing cyclopentane is therefore inferior to those employing conventional HCFC-141b. Accordingly, there is a need for improving the heat insulation characteristics of such rigid polyurethane foams.

The present invention provides a method of preparing a rigid polyurethane foam from

(1) an organic polyisocyanate comprising an aromatic polyisocyanate,

(2) a polyol comprising a polyether polyol and/or polyester polyol,

(3) a blowing agent, and

(4) a surfactant, a catalyst and other auxiliaries,

characterized in that

the blowing agent (3) is cyclopentane and water,

the polyol (2) is a polyether polyol and/or polyester polyol having poor compatibility with cyclopentane, and

cyclopentane is mixed and dispersed in a polyol premix comprising the components (2) to (4).

The phrase "having poor compatibility with cyclopentane" means that the solubility of cyclopentane in the polyol is 20 g or below, for example 10 g or below, and particularly 5 g or below. The term "solubility" means the number of grams of cyclopentane which are soluble in 100 g of the polyol at 25°C.

5

In order to mix and disperse cyclopentane in the polyol premix, it is preferred to use a stirrer of which circumferential speed is at least 5 m/s. In order to allow the dispersed liquid to exist stably in the tank of the foaming machine, it is preferred to stir the mixture at a circumferential speed of at least 0.5 m/s and circulate the mixture through a static mixer.

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The present invention provides a composition for preparation of a rigid polyurethane foam, comprising

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(1) an aromatic polyisocyanate,

(2) a polyether polyol and/or polyester polyol,

(3) a blowing agent comprising a mixture of cyclopentane and water, and

20

(4) a catalyst, a surfactant and other auxiliaries,

and further provides a method of preparing a rigid polyurethane foam from said composition by mechanically disperse cyclopentane in the polyol premix comprising the components (2), (3) and (4).

25

As the aromatic polyisocyanate (1), for example, polyisocyanates such as tolylene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), and polymethylene polyphenyl polyisocyanate (polymeric MDI), or modified polyisocyanates thereof can be used alone or in combination with each other.

30

Modified polyisocyanates, that is, products obtained by partial chemical reactions of organic di- and/or polyisocyanates may be used. For example, di- and/or polyisocyanates containing an ester, urea, biuret, allophanate, carbodiimide, isocyanurate and/or urethane group can be used.

5

The NCO content of the aromatic polyisocyanate (1) is preferably 30 to 50% by weight, for example, 30 to 33% by weight.

The polyol (2) is a polyether polyol and/or polyester polyol.

10

The polyether polyol may be obtained by addition polymerization of propylene oxide and/or ethylene oxide using a polyhydric alcohol such as ethylene glycol, propylene glycol, glycerine, trimethylolpropane, pentaerythritol, sorbitol, sucrose, or bisphenol A, an aliphatic amine such as triethanolamine or ethylenediamine, or an aromatic amine such as toluenediamine or methylenedianiline (MDA) as a starting material.

15

The polyether polyol may be obtained by a known method, for example, by anionic polymerization of an alkylene oxide using a starting material containing 2 to 8, preferably 3 to 8, reactive hydrogen atoms in its molecule, with using an alkali hydroxide such as potassium hydroxide or sodium hydroxide or an alkali alcoholate such as potassium methylate or sodium methylate as a catalyst. Alternatively, the polyether polyol may also be obtained by cationic polymerization of an alkylene oxide using a Lewis acid such as antimony pentachloride or boron fluoride etherate as a catalyst.

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Suitable alkylene oxides are tetrahydrofuran, ethylene oxide, 1,3-propylene oxide, 1,2- or 2,3-butylene oxide, 1,2-propylene oxide, and styrene oxide. Ethylene oxide and 1,2-propylene oxide are particularly preferred. These alkylene oxides may be used alone or a mixture thereof.

30

Examples of the reaction starting material are polyhydric alcohols such as ethylene glycol, propylene glycol, glycerin, trimethylolpropane, pentaerythritol, sorbitol, sucrose, and bisphenol A, or alkanolamines such as ethanolamine, diethanolamine, N-methyl- and N-ethyl-ethanolamine, N-methyl- and N-ethyl-diethanolamine, tri-
5 ethanolamine, and ammonia.

In addition, aliphatic amines and aromatic amines may be used as the reaction starting material. Examples are ethylenediamine, diethylenetriamine, 1,3-propylenediamine, 1,3- or 1,4-butylenediamine, 1,2-, 1,3-, 1,4-, 1,5-, and 1,6-hexamethylenediamine, phenylenediamine, o-toluenediamine, m-toluenediamine, methylenedianiline (MDA), and polymethylenedianiline (P-MDA).
10

The polyether polyol preferably contains 3 to 8, especially preferably 3 to 6, functional groups, and those having a hydroxyl value of 300-800 mg KOH/g, more preferably of 300-500 mg KOH/g, are suitable.
15

As the polyester polyol, a polyester polyol prepared from a polycarboxylic acid and a polyhydric alcohol, such as polyethylene terephthalate, can be used. A suitable polyester polyol may be prepared from an organic carboxylic acid (particularly dicarboxylic acid) having 2-12 carbon atoms and a diol preferably having 2-12 carbon atoms, especially preferably 2-6 carbon atoms.
20

Examples of such organic carboxylic acid are succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, decanedicarboxylic acid, maleic acid, phthalic acid, isophthalic acid, and terephthalic acid. Instead of a free carboxylic acid, corresponding carboxylic acid derivatives, for example dicarboxylic acid monoester or diester of an alcohol having 1-4 carbon atoms or dicarboxylic anhydride, may also be used.
25

As the diol, ethylene glycol, diethylene glycol, 1,2- or 1,3-propanediol, dipropylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, or 1,10-decanediol may be
30

used, and glycerine or trimethylolpropane may be used as a triol. Similarly, lactone-based polyester polyols may also be used.

5 The polyester polyol preferably contains 2 to 3, especially preferably 2, functional groups, and those having a hydroxyl value of 200-600 mg KOH/g, preferably of 350-450 mg KOH/g, are suitable.

10 It is preferred that at least part of the polyol, in particular at least 10% by weight of the polyol, for example at least 30% by weight, is a polyether polyol prepared by addition polymerization of ethylene oxide and propylene oxide to an initiator such as sorbitol.

15 As the blowing agent (3), a combination of cyclopentane and water is used. The amount of water used herein is 0.1 to 5 parts by weight, preferably 0.1 to 1 part by weight, per 100 parts by weight of the polyol. The amount of cyclopentane is preferably 5 to 30 parts by weight, more preferably 10 to 25 parts by weight, per 100 parts by weight of the polyol.

20 As the catalyst, the surfactant and other auxiliaries, those conventionally known may be used. Amine catalysts or metal catalysts may be used as the catalyst.

25 As the amine catalyst, a tertiary amine such as triethylenediamine, tetramethylhexamethylenediamine, pentamethyldiethylenetriamine, or methylmorpholine can be used.

30 As the metal catalyst, an organic metal compound such as stannous octoate, dibutyltin dilaurate, or lead octylate can be used. The amount of the catalyst is preferably 0.01 to 5 parts by weight, more preferably 0.05 to 2.5 parts by weight, per 100 parts by weight of the polyol.

As the surfactant, usual organic silicone-based compounds may be used. For example, L6900, SZ-1684, SZ-1689 or the like manufactured by Nihon Unicar Company Limited, F395 or the like of Shin-Etsu Chemical Co., Ltd., or B8465, B8474 or the like available from Goldschmidt may be used. The amount of the surfactant is 0 to 5 parts by weight, preferably 0.5 to 3 parts by weight, per 100 parts by weight of the polyol.

In the present invention, other auxiliaries such as foaming stabilizers, foam controlling agents, fillers, dyes, pigments, flame retardant additives, anti-hydrolysis agents may be used in appropriate amounts.

For preparation of polyurethane foam, the polyisocyanate and the polyol premix are injected into a mold to harden using a high pressure foaming machine. The NCO index of the polyisocyanate and the polyol premix may be 90 to 150, for example, 110 to 130.

Preferably, the high pressure foaming machine has a circulating line (for example, a high pressure circulating line) and a polyol tank.

The polyol premix is a mixture prepared by adding cyclopentane to a mixture of the polyol, the surfactant, the catalyst, water as a blowing agent and other auxiliaries, and mechanically mixing and dispersing them.

Although the stirrer for mechanically stirring the polyol premix may be any of usual stirrers, those having a circumferential speed of at least 5 m/s is preferred.

For example, cyclopentane may be mechanically mixed and dispersed by a stirrer having stirring wings of 7 cm in diameter at 1700 rpm (circumferential speed: 6 m/s), and fed into the polyol tank of a cyclopentane-compatible high pressure foaming machine having a static mixer in the high pressure circulating line.

A commercially available static mixer is sufficient for this purpose, and for example, a 1 inch x 8 blocks static mixer available from SULZER Corporation may be used.

5 On the other hand, the polyol dispersion liquid can stably exist by reasons that the circumferential speed of the stirrer of the polyol tank is at least 0.5 m/s and the circulating line of the high pressure foaming machine contains the static mixer.

10 By using such high pressure foaming machine, rigid polyurethane foams may be prepared by a prepolymer process or a one-shot process using a batch method or a continuous method. One particularly preferred method is a method of processing conducted according to a two-components process (Component A: isocyanate, Component B: polyol premix).

15 Components A and B are mixed at a temperature in the range of 15 to 35°C, and injected into a mold thermoregulated at 20 to 60°C (for example, 35 to 45°C), and foamed to give a rigid polyurethane foam.

20 The rigid polyurethane foam may be used as heat insulation materials for freezer, refrigerator, building and the like.

The present invention is further demonstrated by the following Examples and Comparative Examples.

5

Cyclopentane Compatibility

Into a test tube, 100 g of a polyol is placed, a given amount of cyclopentane is added, and stirred and mixed thoroughly. After allowing to stand for one day, it is observed whether the mixture is clear, cloudy or separated. When the mixture is clear, the
10 evaluation is "soluble". When the mixture is cloudy or separated, the evaluation is "insoluble".

Compression Strength

The measurement is conducted using a universal tester (TCM 1000 manufactured by
15 Minebea Co., Ltd.) according to JIS-A-9514.

Core Foam Density

The core foam density refers to the density at the central part of the foam, and is calculated by measuring the weight down to 0.01 g and measuring the volume down
20 to 0.1 cm³ by a water displacement method.

Thermal Conductivity

The measurement is conducted on a 200 mm × 200 mm × 25 mm sample cut from the core of the foam, using a thermal conductivity tester (Auto Lambda manufactured
25 by EIKO Instruments Trading, Co.) according to ASTM-C-518.

Example 1

A polyol mixture liquid was prepared by adding an amine catalyst (1.8 parts by weight of tetramethylhexamethylenediamine plus 1.0 part by weight of pentamethyl-diethylenetriamine plus 0.5 part by weight of trisdimethylaminopropyl-s-triazine), 2 parts by weight of a surfactant (L6900 manufactured by Nihon Unicar Company Limited), and 0.5 part by weight of water to 30 parts by weight of Polyol A, 25 parts by weight of Polyol B, 20 parts by weight of Polyol C, 20 parts by weight of Polyol D, and 10 parts by weight of Polyol E.

To the polyol mixture liquid, 21 parts by weight of cyclopentane (blowing agent), was added, and mechanically mixed and dispersed by a stirrer having 7-cm stirring wings at 2,000 revolutions/min (circumferential speed: 7 m/s) to prepare the final polyol mixture. The polyol mixture liquid was fed into a high pressure foaming machine equipped with a static mixer (a 1 inch x 8 blocks mixer manufactured by SULZER Corporation), and mixed by circulating it at high pressure for a while. The solubility of cyclopentane was 5 g or below per 100 g of the polyols.

According to the mixing ratio shown in Table 1, the polyol mixture and polymeric MDI were mixed and foamed. The urethane feedstocks were adjusted at the temperature of 20°C, and injected into a 600 mm x 400 mm x 50 mm aluminum mold adjusted at 45°C, and the molded product was demolded from the mold after 7 minutes. Physical properties of the molded product are shown in Table 1.

Examples 2 and 3

A polyol mixture liquid was prepared according to Table 1. As a silicone-containing surfactant, 2 parts by weight of F395 manufactured by Shin-Etsu Chemical Co., Ltd. was used. The other procedures were the same as those described in Example 1. Physical properties of the molded product are shown in Table 1.

Comparative Examples 1 and 2

As in Example 1, a polyol mixture liquid was prepared according to Table 1. The mixture liquid was then mixed with cyclopentane, and fed into the high pressure foaming machine, and the molded product was obtained in the same manner as in Example 1. The difference between these Comparative Examples and Examples 1-3 is in that the polyol mixture liquid in these Comparative Examples was a liquid in which cyclopentane was completely dissolved. Physical properties of the molded product are shown in Table 1.

Polyol A:

A polyol obtained by addition of EO (ethylene oxide) and PO (propylene oxide) to sorbitol as a starting material, having a hydroxyl value of 550 mg KOH/g

Polyol B:

A polyol obtained by addition of PO to glycerin as a starting material, having a hydroxyl value of 520 mg KOH/g

Polyol C:

A polyol obtained by addition of EO to trimethylolpropane as a starting material, having a hydroxyl value of 550 mg KOH/g

Polyol D:

A polyol obtained by addition of PO to trimethylolpropane as a starting material, having a hydroxyl value of 865 mg KOH/g

Polyol E:

A polyester polyol derived from polyethylene terephthalate, having a hydroxyl value of 315 mg KOH/g

Polyol F:

A polyol obtained by addition of EO to ethylene glycol as a starting material, having a hydroxyl value of 374 mg KOH/g

5 Polyol G:

A polyester polyol derived from phthalic acid and diethylene glycol, having a hydroxyl value of 420 mg KOH/g

Polyol H:

10 Glycerin

Polyol J:

A polyol obtained by addition of PO to glycerin as a starting material, having a hydroxyl value of 390 mg KOH/g

15

Polyol K:

A polyol obtained by addition of PO to toluenediamine/diethanolamine as starting materials, having a hydroxyl value of 450 mg KOH/g

20 Polyol L:

A polyol obtained by addition of PO to sugar/propylene glycol as starting materials, having a hydroxyl value of 380 mg KOH/g

Polyol M:

25 A polyol obtained by addition of PO to propylene glycol as a starting material, having a hydroxyl value of 500 mg KOH/g

Table 1

| | Example 1 | Example 2 | Example 3 | Comparative Example 1 | Comparative Example 2 |
|--|--------------------|--------------------|--------------------|--------------------------|--------------------------|
| Polyol A | 30 | 35 | 30 | - | - |
| Polyol B | 25 | - | 25 | - | - |
| Polyol C | 25 | - | - | - | - |
| Polyol D | 10 | - | - | - | - |
| Polyol E | 10 | - | - | - | - |
| Polyol F | - | 20 | 20 | - | - |
| Polyol G | - | 20 | 20 | 15 | - |
| Polyol H | - | 5 | 5 | - | - |
| Polyol J | - | 20 | - | - | - |
| Polyol K | - | - | - | 40 | 50 |
| Polyol L | - | - | - | 45 | 40 |
| Polyol M | - | - | - | - | 10 |
| Cyclopentane | 21 | 21.5 | 21.5 | 15.5 | 11.2 |
| water | 0.5 | 0.5 | 0.6 | 1.3 | 2.0 |
| Polymeric MDI | 170 | 130 | 130 | 123 | 140 |
| Compressive strength (kg/cm ²) | 2.0 | 1.5 | 1.6 | 1.5 | 2.0 |
| Core foam density (kg/m ³) | 35 | 32 | 32 | 32 | 35 |
| Thermal conductivity × 10 ⁻⁴ (kcal/mh°C) | | | | | |
| 25°C | 163 | 161 | 162 | 163 | 173 |
| 10°C | 154 | 155 | 156 | 158 | 168 |
| 0°C | 150 | 151 | 152 | 156 | 166 |
| Pentane compatibility (solubility: g) | Insoluble, ≤5 g | Insoluble, ≤5 g | Insoluble, ≤5 g | Soluble | Soluble |

- 5 According to the present invention, a rigid polyurethane foam having a low thermal conductivity and excellent heat insulating properties can be prepared by using polyols having poor compatibility with cyclopentane.

Claims

1. A method of preparing a rigid polyurethane foam from

5 (1) an organic polyisocyanate comprising an aromatic polyisocyanate,

(2) a polyol comprising a polyether polyol and/or polyester polyol,

(3) a blowing agent, and

10

(4) a surfactant, a catalyst and other auxiliaries,

characterized in that

15

the blowing agent (3) is cyclopentane and water,

the polyol (2) is a polyether polyol and/or polyester polyol having
poor compatibility with cyclopentane, and

20

cyclopentane is mixed and dispersed in a polyol premix comprising
the components (2) to (4).

2. A method of claim 1 characterized in that a high pressure circulating line
equipped with a static mixer is used to mix and disperse cyclopentane.

25

3. A method of claim 1 characterized in that at least part of the polyol is a
polyether polyol prepared by addition polymerization of ethylene oxide and
propylene oxide to an initiator.

30

4. An apparatus for preparing a rigid polyurethane foam, used in the method of
claim 1, characterized in that it comprises a static mixer in a high pressure

circulating line for mixing and dispersing cyclopentane, and the circumferential speed of a stirrer of a polyol tank is at least 0.5 m/s.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/07691

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08J9/14 B29C44/34 C08J9/30 //C08L75/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08J B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | DE 197 08 570 A (BASF AG) 10 September 1998 (1998-09-10) | 1-3 |
| Y | Comparative example 1 claims | 4 |
| Y | US 4 275 172 A (BARTH BRUCE P ET AL) 23 June 1981 (1981-06-23) column 3, line 39-45 claims | 4 |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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Date of the actual completion of the international search

10 February 2000

Date of mailing of the international search report

18/02/2000

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/07691

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| DE 19708570 A | 10-09-1998 | NONE | |
| US 4275172 A | 23-06-1981 | CA 1161994 A | 07-02-1984 |

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

| | | |
|--|---|--|
| Applicant's or agent's file reference SBU 114-W0 | FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below. | |
| International application No. PCT/EP 99/07691 | International filing date (day/month/year) 13/10/1999 | (Earliest) Priority Date (day/month/year) 26/10/1998 |
| Applicant BAYER AKTIENGESELLSCHAFT et al. | | |

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2. ☐ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (see Box II).

4. With regard to the title,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of the international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/07691

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| DE 19708570 A | 10-09-1998 | NONE | |
| US 4275172 A | 23-06-1981 | CA 1161994 A | 07-02-1984 |